

Rupture of Amorphous Polymers*

by

R. F. Landel and R. F. Fedors

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Fracture of elastomers depends simultaneously on many parameters, and, therefore, a comprehensive understanding of fracture requires knowledge of not only their separate effects but also of their interactive effects. Thus, studies have been made on the influence of time¹, temperature¹, degree of crosslinking^{2,3}, details of chain structure^{3,4} and concentration of diluent⁵, but seldom has a sufficiently wide range and combination of such variables been covered in any given experimental program so as to provide an indication of the interactions. In order to synthesize these experimental results into a more coherent whole, fracture in viscoelastic bodies should not be treated as a separate phenomenon, but rather as one facet of the problem of describing their stress-strain-time (σ , ϵ , t) properties⁶. (Only tensile properties are considered here.) If these properties are considered as a three-dimensional surface, which we call a physical property surface, then fracture represents some limiting value or discontinuity on this surface, or boundary to it⁶. Figure 1 depicts such a surface for a gum Viton B elastomer.

* This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

N 66 86807

(ACCESSION NUMBER)

(THRU)

20

None

(PAGES)

(CODE)

CR-68443

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

The projections of this boundary to the σ , t or ϵ , t planes depict the time dependence of fracture, while the projection to the σ , ϵ plane is independent of the time scale. This latter projection, known as the Smith failure envelope, is of great importance because of this independence. Moreover, the failure envelope appears to be independent of the path, so that the same envelope is generated in stress relaxation^{6,7,8}, creep⁸, or constant strain rate^{6,7,8} experiments. As such it serves as a very useful failure criterion.

Thus, in mathematical terms, a useful description of fracture behavior requires at least two functions which can be solved simultaneously to yield values of σ , ϵ and t at break. A possible pair of such functions, for example, would be the set comprised of one expression for the property surface and one expression relating ϵ_b to t_b .

There is ample experimental evidence to suggest that over much of the property surface, strain and time are factorable⁹ so that the equation for the surface may be written as:

$$\sigma = E(t) f(\epsilon, n) \quad (1)$$

where $E(t)$ is the time dependent, strain independent modulus. At long times, E approaches equilibrium and becomes time independent; here kinetic theory predicts $E(eq) = 3 \nu_e RT$. $f(\epsilon, n)$ is generally a nonlinear function of strain which is independent of time. The function f however also depends on a parameter n which is a measure of chain flexibility.

A possible form for the function $f(\epsilon, n)$ which fits data very well has been proposed by Treloar¹⁰, and is based on an extension of the kinetic theory of rubberlike elasticity which takes into account finite extensibilities of a polymer chain:

$$f(\epsilon, n) = \frac{n^{\frac{1}{2}}}{q} \left[\mathcal{L}^{-1}\left(\frac{\lambda}{n^{\frac{1}{2}}}\right) - \frac{1}{\lambda^{3/2}} \mathcal{L}^{-1}\left(\frac{1}{\lambda^{\frac{1}{2}} n^{\frac{1}{2}}}\right) \right] \quad (2)$$

where $\lambda = \epsilon + 1$ and where \mathcal{L}^{-1} is the inverse Langevin function, e.g., if

$$\mathcal{L}^{-1}\left(\frac{\lambda}{n^{\frac{1}{2}}}\right) = \beta$$

then

$$\frac{\lambda}{n^{\frac{1}{2}}} = \coth \beta - \frac{1}{\beta} = \mathcal{L}(\beta)$$

In (2), it is easy to show that $f(\epsilon, n) \rightarrow \infty$ as $\lambda \rightarrow n^{1/2}$ and thus, the magnitude of n provides an upper limit to the maximum value which λ can attain. Thus, if eqn. (2) is valid for values at break, then

$$(\lambda_b)_{\max} = n^{\frac{1}{2}} \quad (3)$$

where $(\lambda_o)_{\max}$ is the maximum value of λ_o as obtained from the upturn in the failure envelope at the point where $\frac{d\sigma_o}{d\epsilon} = \infty$. Equation (3) can be recast into the more convenient form:

$$(\lambda_b)_{\max} = \left[\frac{q}{v_e N \left(1 + \frac{\rho q}{v_e M n}\right)} \right]^{\frac{1}{2}} \quad (4)$$

where g is the gel fraction, N is the molar volume of a statistical unit, ρ is the density and \bar{M}_n is the number average molecular weight of the primary molecules. When \bar{M}_n is large, the factor in parenthesis approaches unity and $(\lambda_b)_{\max}$ becomes inversely proportional to $\nu_e^{1/2}$. There is experimental data³ to support this type of dependence on ν_e .

In addition, when $\lambda \ll n^{1/2}$, equation (2) becomes essentially independent of n and hence the effect of n on f becomes apparent primarily when $\lambda \rightarrow n^{1/2}$. To indicate how well (2) applies to break data, figure 2 shows rupture data obtained with SBR gum at the indicated rates and temperatures. The line shown in equation (2) with $n = 50$.

Experimentally, it has been observed⁶ that in the ϵ_b, t_b plane, ϵ_b depends on both t_b and n i.e.,

$$\epsilon_b = g(t_b, n) \quad (5)$$

Hence, equations (1) and (5) considered together define a space curve on the property surface which defines fracture for all experimental conditions for which (1) remains valid.

Differentiation and rearrangement of equations (1) and (5) yield an equation which defines the shape and location of the failure envelope in the σ_b, ϵ_b plane:

$$\frac{d\sigma_b}{d\epsilon_b} = f \frac{\left(\frac{\partial E}{\partial t_b}\right)}{\left(\frac{\partial g}{\partial t_b}\right)} + \left[E \frac{\partial f}{\partial n} - f \left(\frac{\partial g}{\partial n}\right) \frac{\left(\frac{\partial E}{\partial t_b}\right)}{\left(\frac{\partial g}{\partial t_b}\right)} \right] \frac{dn}{d\epsilon_b} + E \left(\frac{\partial f}{\partial \epsilon_b}\right) \quad (6)$$

Equation (6) predicts that the shape of the failure envelope depends on many variables simultaneously in a rather complicated fashion. It is interesting to note that since the failure envelope is independent of time, the left-hand side of (6) can only be a function of f and n . This implies that functional relations must exist between the quantities in (6) which are time dependent. If the explicit expressions for E , g and f were known, equation (6) in principle could be integrated to yield the mathematical expression for the envelope.

Fortunately, over a rather wide range of temperature, $E(t)$ is only a very slowly varying function of time which, hence, can be taken as constant and set equal to its kinetic theory value of $3\nu_e RT$. Under these conditions, (6) becomes

$$\frac{d\sigma_b}{d\epsilon_b} = 3\nu_e RT \left[\left(\frac{\partial f}{\partial n} \right) \left(\frac{\partial n}{\partial \epsilon_b} \right) + \frac{\partial f}{\partial \epsilon_b} \right] \quad (7)$$

Thus for those conditions under which E can be taken as constant, (7) predicts that the shape of the envelope depends only on f and on its variation with both ϵ_b and n and on the variation of n with respect to ϵ_b . Furthermore, the dependence of the envelope on ν_e can be removed by normalizing σ_b to unit ν_e , i.e.,

$$\frac{d \left(\frac{\sigma_b}{\nu_e RT} \right)}{d\epsilon_b} = 3R \left[\left(\frac{\partial f}{\partial n} \right) \left(\frac{\partial n}{\partial \epsilon_b} \right) + \frac{\partial f}{\partial \epsilon_b} \right] \quad (8)$$

In addition, since for small values of the ratio, ϵ_b/n , f is essentially independent of n , then (8) becomes

$$\frac{d\left(\frac{\sigma_b}{\nu_e T}\right)}{d\epsilon_b} = 3R \left[\frac{2f}{2\epsilon_b} \right] \quad (9)$$

which can be integrated directly to yield

$$\frac{\sigma_b}{\nu_e T} = 3R f(\epsilon) \quad (10)$$

It has been shown previously^{3,6} that when the breaking stress is normalized to unit ν_e , then at temperatures sufficiently above the glass temperature, the reduced stress is a unique function of the breaking strain, independent of the chemical structure of the chain (epoxy, silicone, butadiene, butyl, fluorocarbon, styrene-butadiene), such that data for some fifteen elastomers can be reduced to a single master curve as predicted by equation (10).

In figure 3a, the rupture data, obtained at a single rate and temperature, are shown for four elastomers which vary in both chemical structure and crosslink density. When these data are reduced to unit crosslink density as suggested by equation (8) or (10), the data superpose to a single curve to within the experimental uncertainty in the reported ν_e values. The line shown in figure 3b represents the average behavior for this set of data.

As a more clear-cut demonstration of the independence of the reduced master envelope and chemical structure, figure 4a shows the failure envelopes for five types of rubber, each at a constant crosslink density. These envelopes were obtained by making tests at several strain rates and temperatures. As the temperature is lowered or the strain rate is increased, the data points move counter-clockwise around the envelope. When these envelopes are reduced, as in figure 4b, their high temperature portions superpose as expected, even though ν_e varies by a factor of 40.

It might be argued that, since not only ν_e but T_g and type of backbone are being changed, the reduction is not real but only an artifact stemming from the simultaneous change in several variables. Hence we offer the evidence based on a single rubber, Viton A-HV, as measured by Smith². Figure 5a is a plot of his tabulated rupture data, the crosslink densities being given in the key. Figure 5b shows the reduced failure envelope and it can be seen that the high temperature portions have all merged into a common response curve, independent of ν_e .

The master envelope or common response curve is statistical variation; in the rupture properties. Hence, independent of statistical variations in the breaking properties as measured for a sample of a given crosslink density at a given strain rate and temperature, permit the delineation of portions of the failure envelope for that sample. This is illustrated in figure 6a, where the unfilled squares show portions of the envelope for an SBR rubber as measured at these different temperatures, compared to the envelope formed by varying the strain rate and temperature (the solid line). The filled squares denote the segments formed at 25°C¹¹ at progressively lower crosslink densities. In figure 6b, these data have

been reduced to unit ν_e and compared with the reduced master curve (solid line) obtained earlier. Again, the reduction principle holds at high temperatures and hence is unaffected by statistical variability.

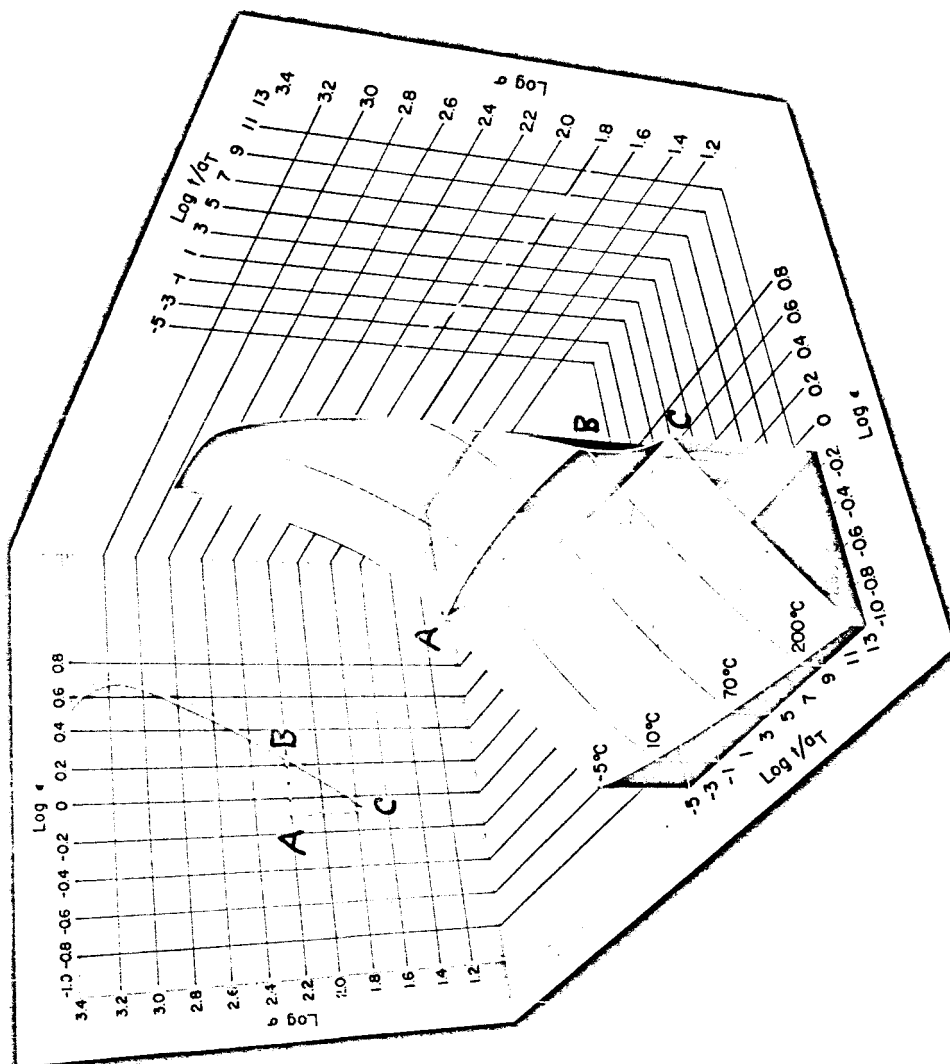
Figure 7 shows the reduced failure envelopes for all the systems discussed here. The high temperature portions of all envelopes have been brought together into a master curve which is essentially the same one shown earlier. Thus the reduced variable concept as proposed is valid for wide ranges in polymer-type, T_g , crosslink density, test rate, test temperature, and statistical fluctuations in the data.

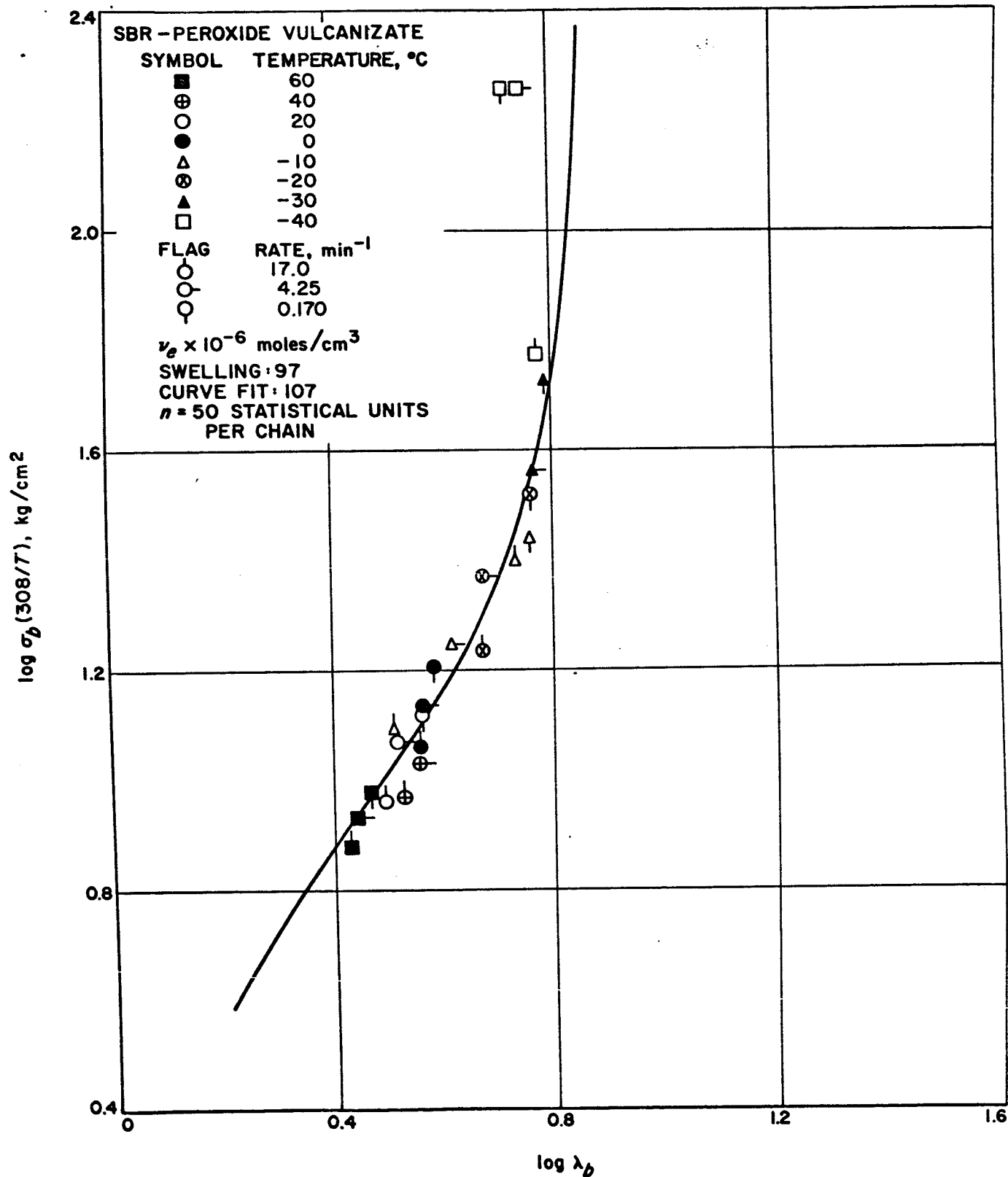
Conclusions

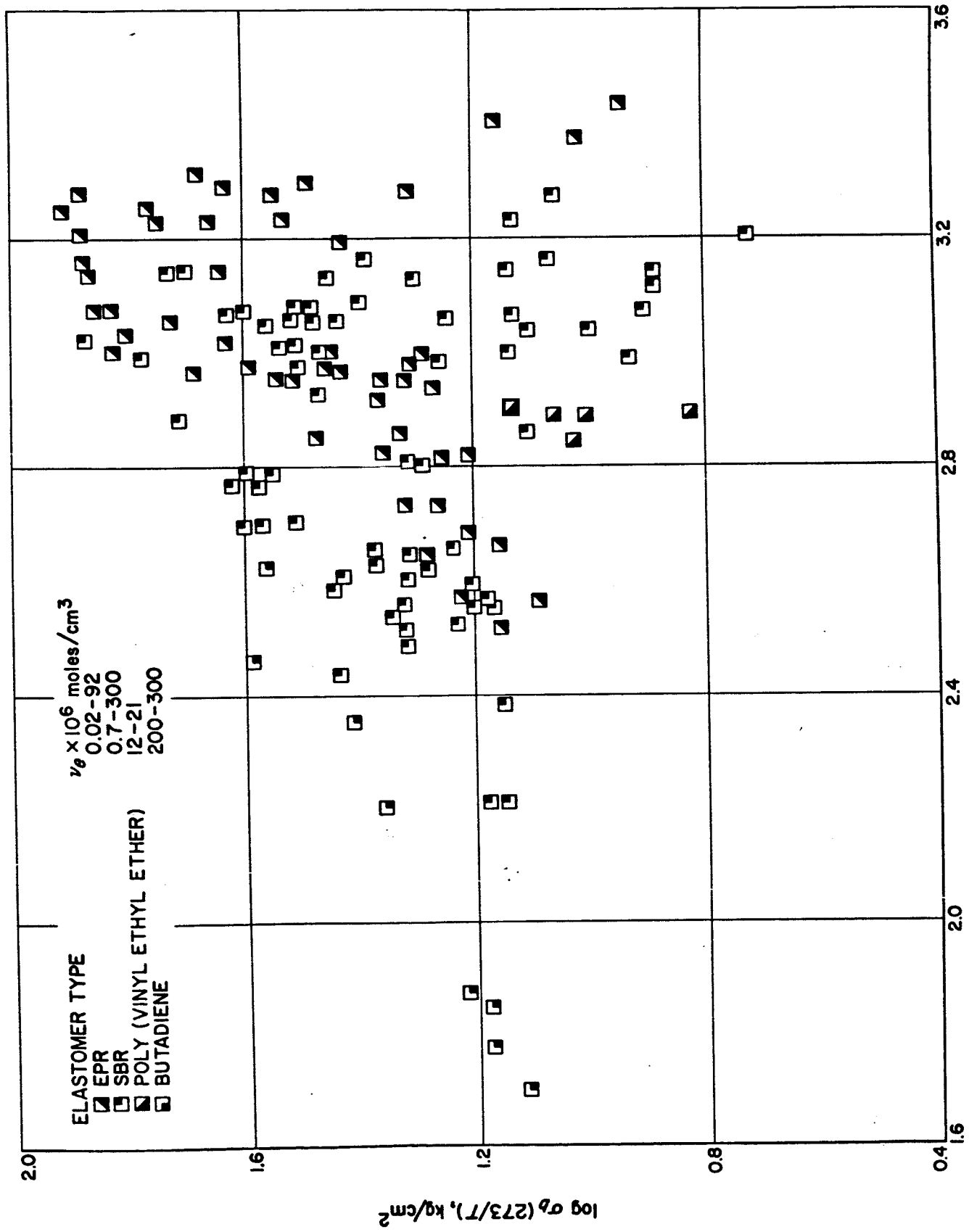
At sufficiently high temperatures compared to the glass temperature, both experimental evidence (figure 7) and equation (10) predict that failure envelopes obtained from samples differing in ν_e will superpose to a common response curve $f(\epsilon)$ independent of chemical structure of the polymer when σ_b is normalized to unit $\nu_e T$. At lower temperatures, experiment and equation (8) indicate that in such a normalized plot, individual failure envelopes will diverge from the common response curve, $f(\epsilon)$, due primarily to the influence of the chain flexibility lowered parameter n . As the temperature is still further, equation (6) shows that the shapes of individual envelopes may vary if the time dependences of E and/or g differ. This effect is presumably the factor which produces the difference in shapes between the Viton elastomers and the others shown in figure 7. In addition, equation (4) relates the maximum value which λ_b can attain to other readily measured parameters, notably ν_e . Thus the knowledge of these two parameters, ν_e and n is sufficient to predict to a good approximation the shape and location of the failure envelope up to the region of $(\lambda_b)_{\max}$.

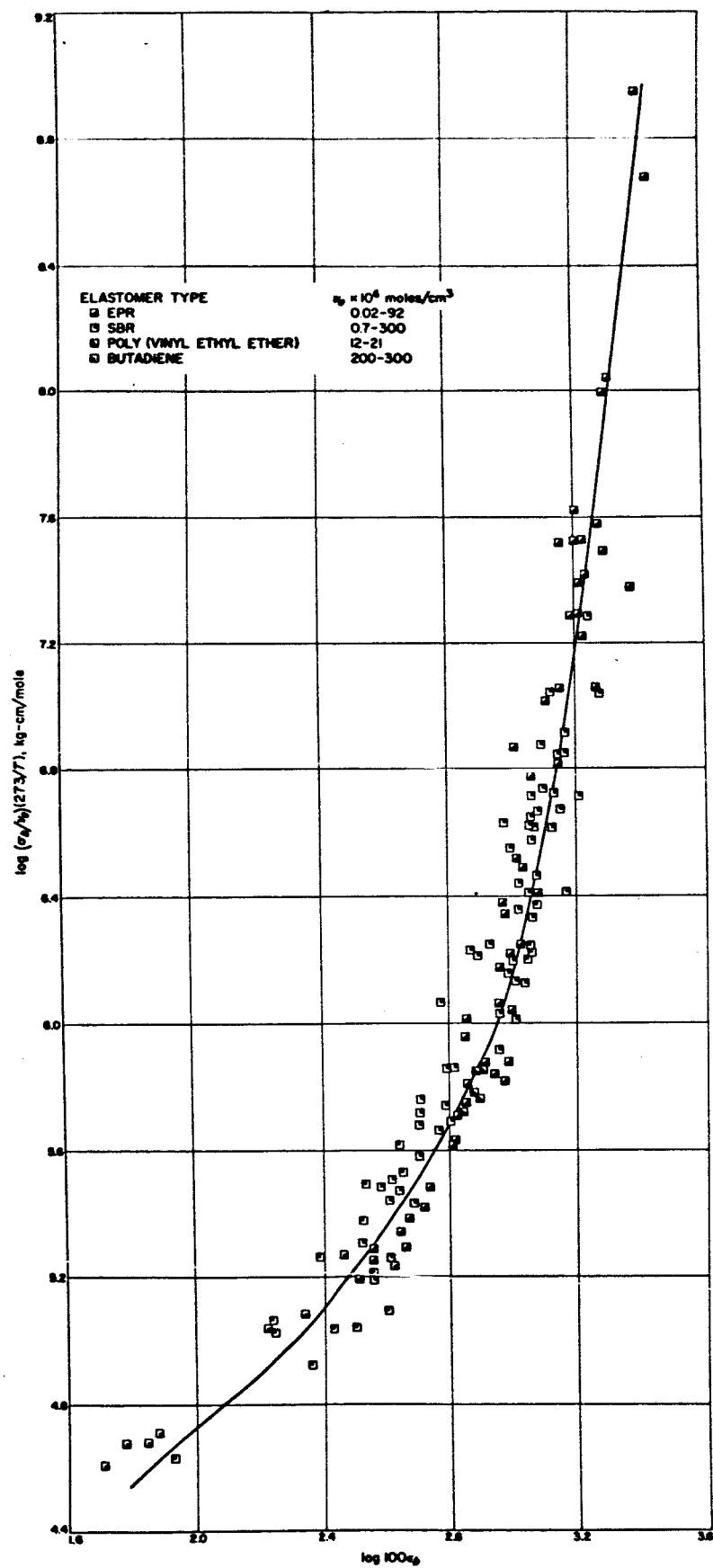
References

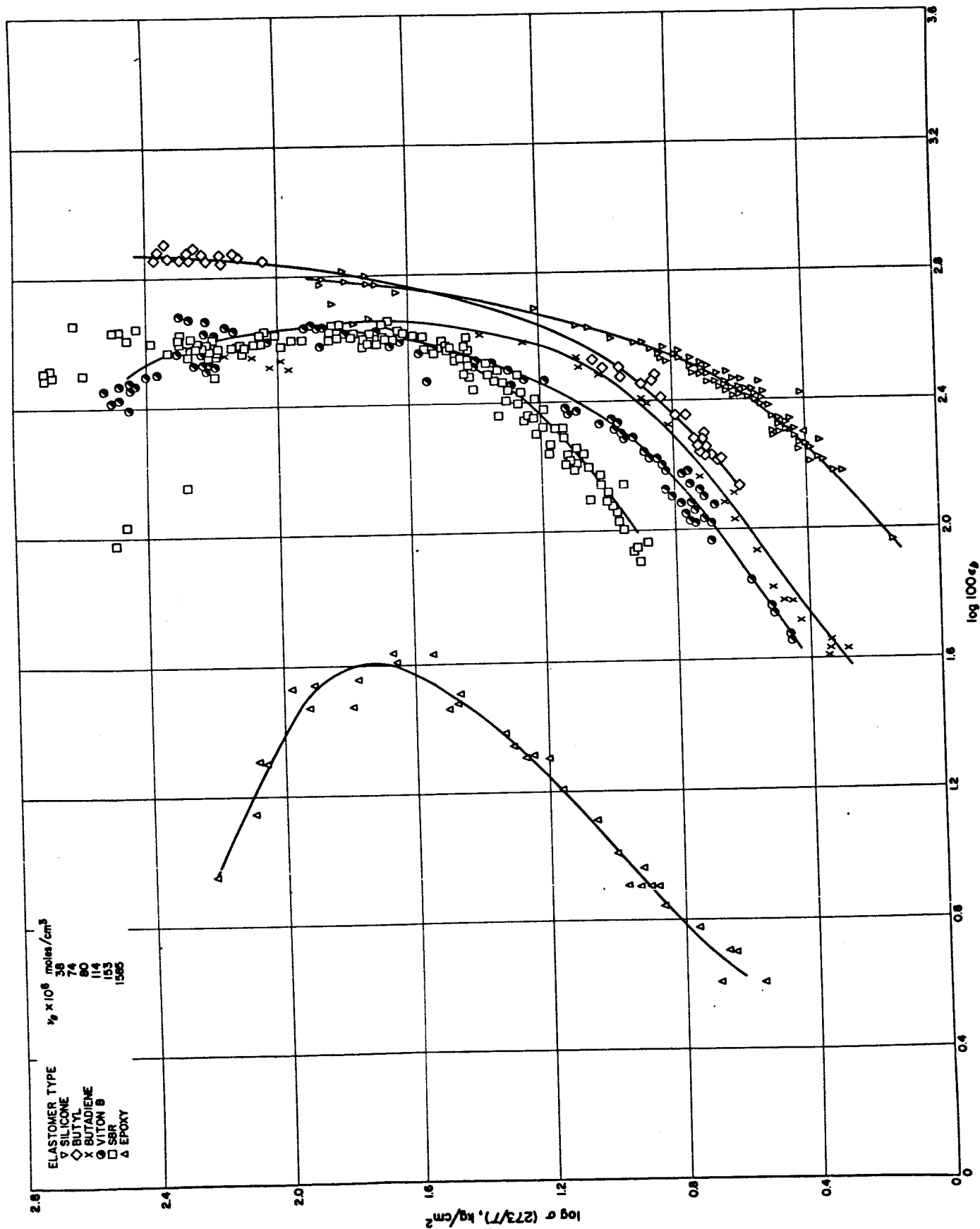
1. Smith, T. L., J. Polymer Sci., 32, 99 (1958).
2. Smith, T. L., Proceedings of the Fourth International Congress on Rheology, Part 2, E. H. Lee, editor, Interscience Publishers, New York (1965), p. 525.
3. Landel, R. F., and Fedors, R. F., ibid, p. 543.
4. Smith, T. L., J. Appl. Phys., 35, 27 (1964).
5. Epstein, L. M., and Smith, R. P., Trans. Soc. Rheology, 2, 219 (1958).
6. Landel, R. F., and Fedors, R. F., Fracture Processes in Polymeric Solids, Phenomena and Theory, B. Rosen, editor, Interscience Publishers, New York (1964), Chapter IIIB.
7. Smith, T. L., J. Polymer Sci., 1, 3597 (1963).
8. Halpin, J. C., J. Appl. Physics, 35, 3133 (1964).
9. Landel, R. F., and Stedry, P., J. Appl. Physics, 31, 1885 (1960).
10. Treloar, L. R. G., The Physics of Rubber Elasticity, Clarendon Press (1958), Chapter 6.
11. Fedors, R. F., and Landel, R. F., Trans. Soc. Rheology, 2, 195 (1965).

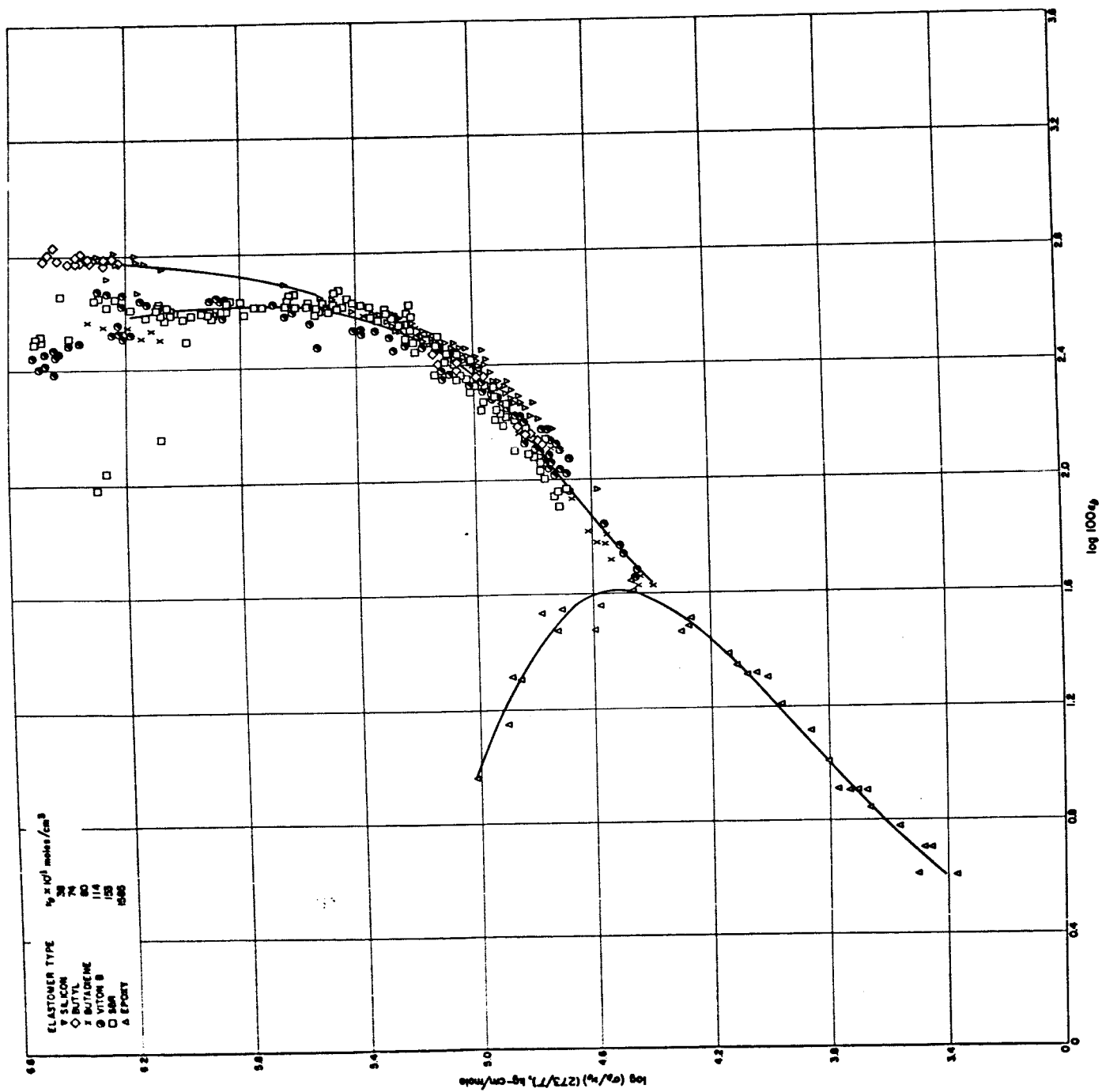


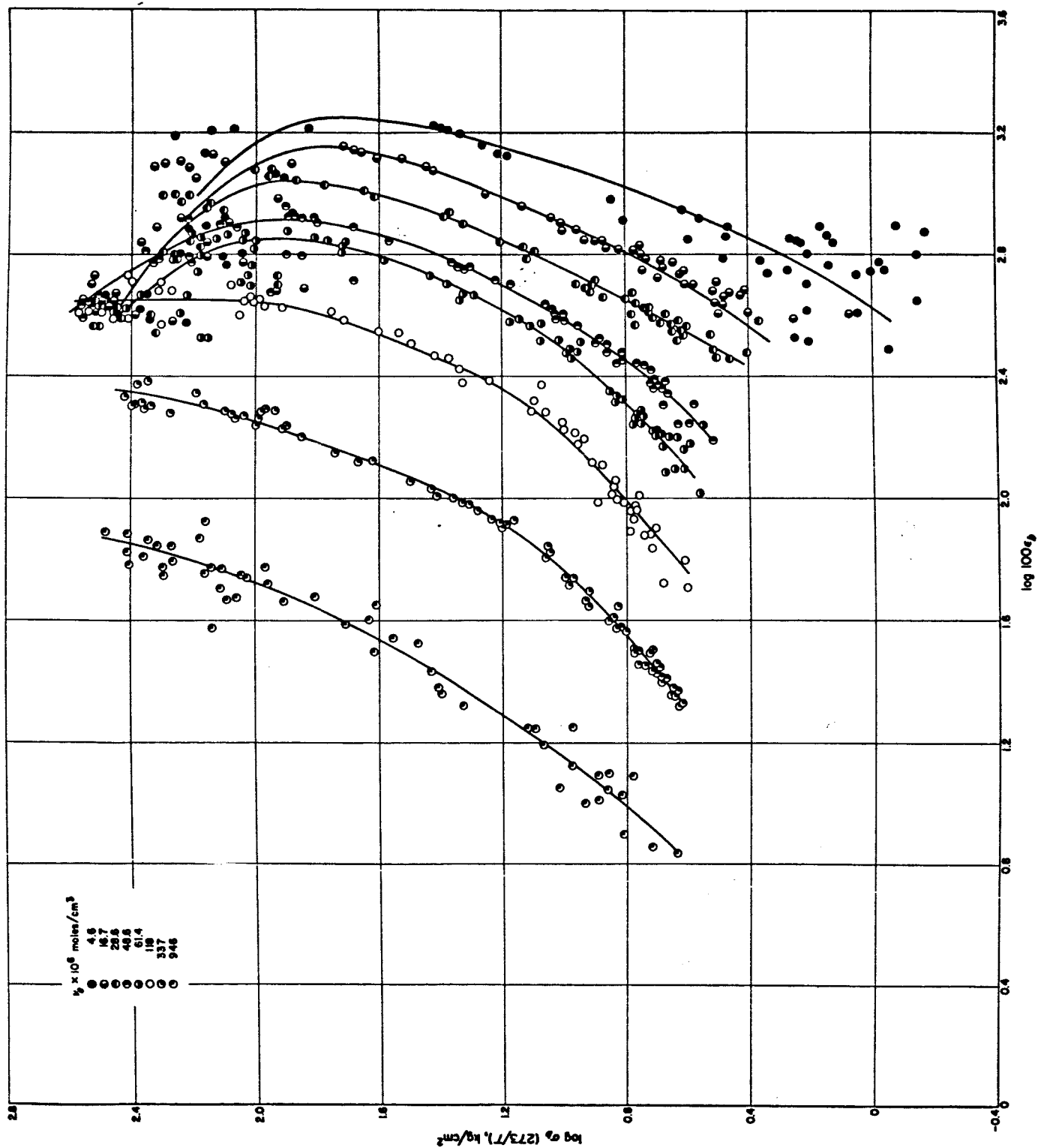


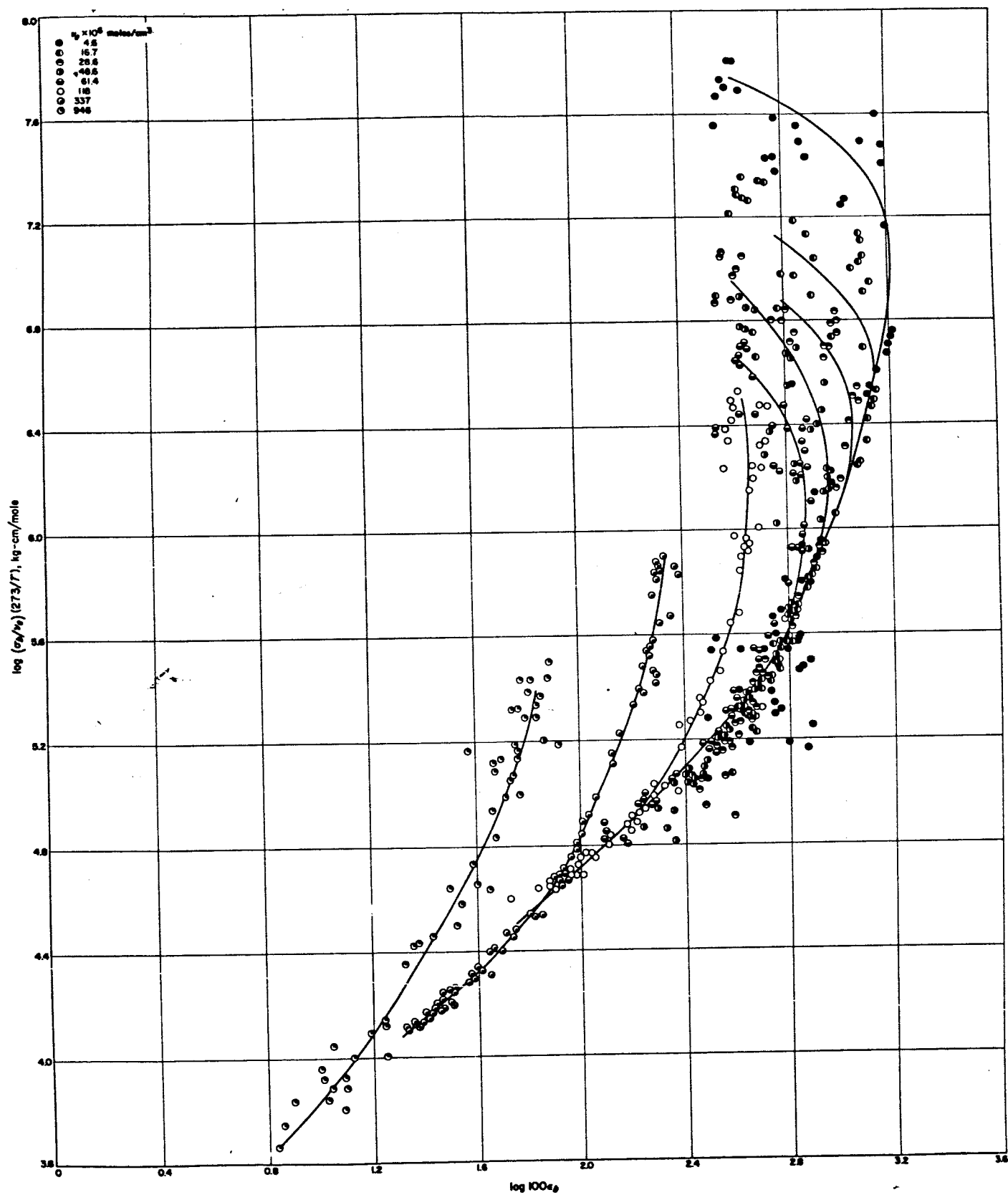












6a

